

Application of self-consistent α method to improve the performance of model exchange potentials

Valentin V. Karasiev,^{1,*} Eduardo V. Ludeña,¹ and Artëm E. Masunov²

¹*Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 21827, Caracas 1020-A, Venezuela*

²*NanoScience Technology Center, Department of Chemistry and Department of Physics, University of Central Florida, 12424 Research Parkway, Orlando, Florida 32826*

(Dated: 17 October 2009)

Self interaction error remains an important problem in density functional theory. A number of approximations to exact exchange aimed to correct for this error while retaining computational efficiency had been suggested recently. We present a critical comparison between model exchange potentials generated through the application of the asymptotically-adjusted self-consistent α , AASC α , method and BJ effective exchange potential advanced in [A.D. Becke and E.R. Johnson, J. Chem. Phys. 124, 221101 (2006)] and [V.N. Staroverov, J. Chem. Phys. 129, 134103 (2008)]. In particular we discuss their compliance with coordinate-scaling, virial and functional derivative conditions. We discuss the application of the AASC α method to generate the AA-BJ potential. A numerical comparison is carried out through the implementation of a fully-numerical diatomic molecule code yielding molecular virial energies and ionization potentials approximated by the energies of the HOMO orbitals. It is shown that some of the shortcomings of these model potentials, such as the non-compliance with the Levy-Perdew virial relation, may be eliminated by multiplying the response term by an orbital-dependent functional α , which can be simplified to a constant determined during the self-consistent procedure (self-consistent α).

PACS numbers:

I. INTRODUCTION

An important problem arising in the application of the Kohn-Sham equations is that of the construction of the local exact exchange potential. In principle, this potential can be exactly calculated following the procedure outlined in the OEP method. [1–9] However, in practice, there are a number of difficult numerical impediments that bar the way to the realization of this exact approach [10–13] in addition to some deeper problems stemming from general instabilities of Kohn-Sham potentials in finite dimensional subspaces. [13]

For this reason, particularly in recent years, much attention has been devoted to the development of alternative local-exchange potentials which are simple to apply but which at the same time yield sufficiently accurate results. [3, 14–23]

A few years ago, we introduced such an approach, which we called the “asymptotically-adjusted self-consistent α ” (AA-SC α) method. Although the detailed theoretical justification for this method is presented in Ref. [24], we comment here on two of its characteristics.

The first is that in the AA-SC α method the following model potential is postulated:

$$v_x^{\text{AASC}\alpha}(\mathbf{r}) = v_S(\mathbf{r}) + \alpha_x[\{\psi_i\}]\tilde{v}_{\text{resp}}^0(\mathbf{r}) \quad (1)$$

where $v_S(\mathbf{r})$ is the local Slater potential and where $\tilde{v}_{\text{resp}}^0(\mathbf{r}) = v_x^0(\mathbf{r}) - 2\epsilon_x^0([\rho]; \mathbf{r})$ is a local response poten-

tial related to an approximate (and arbitrary) exchange functional $E_x^0[\rho] = \int d^3\mathbf{r}\rho(\mathbf{r})\epsilon_x^0([\rho]; \mathbf{r})$ yielding the local exchange potential $v_x^0(\mathbf{r}) = \delta E_x^0[\rho]/\delta\rho$; (however, more generally, the response term $\tilde{v}_{\text{resp}}^0$ also may be modelled). In Eq. (1), $\alpha_x[\{\psi_i\}]$ is the functional

$$\alpha_x[\{\psi_i\}] = \frac{E_x[\{\psi_i\}] - E_{\text{xLP}}[v_S([\rho]), \rho]}{E_{\text{xLP}}[\tilde{v}_{\text{resp}}^0([\rho]), \rho]} \quad (2)$$

where $E_x[\{\psi_i\}]$ is the exact orbital expression for the exchange energy, and $E_{\text{xLP}}[v([\rho]; \mathbf{r}), \rho(\mathbf{r})] = \int d^3\mathbf{r}v(\mathbf{r})[3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla\rho(\mathbf{r})]$ is the Levy-Perdew expression for the exchange energy functional corresponding to the potential $v(\mathbf{r})$ [25, 26]. The local potential given by Eq. (1) is called “asymptotically adjusted” because while the first term guarantees the correct asymptotic behavior of $-1/r$ for large r the second term does not contribute in the asymptotic region.

The second characteristic follows from Eq. (2):

$$\begin{aligned} E_x[\{\psi_i\}] &= E_{\text{xLP}}[v_S([\rho]), \rho] + \alpha_x[\{\psi_i\}]E_{\text{xLP}}[\tilde{v}_{\text{resp}}^0([\rho]), \rho] \\ &\equiv E_x^{\text{AASC}\alpha}[\{\psi_i\}] \end{aligned} \quad (3)$$

The variational derivative of this functional with respect to the Kohn-Sham orbital yields:

$$\frac{\delta E_x^{\text{AASC}\alpha}[\{\psi_i\}]}{\delta\psi_j} = \left(v_x^{\text{AASC}\alpha}(\mathbf{r}) + \Delta\hat{v}_x(\mathbf{r}) \right) \psi_j(\mathbf{r}) \quad (4)$$

where $\Delta\hat{v}_x(\mathbf{r})\psi_j(\mathbf{r}) = [\hat{v}_{xj}(\mathbf{r}) - v_S(\mathbf{r}) - \alpha_x\tilde{v}_{\text{resp}}^0(\mathbf{r})]\psi_j(\mathbf{r})$ is a non-local correction to the $v_x^{\text{AASC}\alpha}(\mathbf{r})$ potential. It has been shown [24] that the contribution of $\Delta\hat{v}_x(\mathbf{r})$ to the energy is $\Delta E_x[\{\psi_i\}] = 0$ where $\Delta E_x[\{\psi_i\}] =$

*Electronic address: vkarasev@qtp.ufl.edu

$E_x[\{\psi_i\}] - E_{xLP}[v_S] - \alpha_x[\{\psi_i\}]E_{xLP}[\tilde{v}_{\text{resp}}^0]$. Hence, the omission of $\Delta\hat{v}_x(\mathbf{r})$ in the Kohn-Sham equation only affects the quality of the converged orbitals but it does not change the expression for the energy.

The AASC α method has been applied previously to improve the potentials and energies of several DFT exchange functionals. In particular, we have analyzed the improvements brought about by this method with respect to the LDA and PW91 functionals and proposed two models for $\tilde{v}_{\text{resp}}^0$ term [24].

However, quite recently a very simple potential denoted as the BJ effective exchange potential has been proposed in a heuristic way by Becke and Johnson [20]. This potential contains a Slater term plus a local response one. This work has been extended by Staroverov [23] who has advanced a family of model potentials which have the form of a Slater potential plus a response term which is modeled. In all these cases the energy is evaluated using the exact expression $E_x[\{\psi_i\}]$ for the exchange functionals constructed from the N occupied orbitals which have self-consistently converged for the given model potential.

In the present work, due to the similarities between this family of potentials and the AASC α one, we make a critical comparison between these potentials. We also apply the AASC α method using the model exchange functional associated with the BJ potential to generate the AA-BJ one. The systems chosen for the present comparison are some selected diatomic molecules. We show that application of the AASC α method does indeed bring improvements, albeit slight, on both the BJ energies and ionization potentials. Also, we show that it yields internuclear distances that are in excellent agreement with the exact Kohn-Sham x-only results.

II. COMPARISON WITH THE BJ AND RELATED MODELS

There are three formal conditions that the exact optimized effective potential (OEP) for exchange must satisfy [27, 28]. These are: the variational derivative condition, the virial relation, and the scaling requirement.

Quite clearly, the AASC α local potential $v_x^{\text{AASC}\alpha}(\mathbf{r})$ is an approximate one and, hence, it does not satisfy all three of these conditions. As it is shown in Eq. (4), the variational derivative of $E_x^{\text{AASC}\alpha}[\{\psi_i\}]$ with respect to ψ_i yields the potential $v_x^{\text{AASC}\alpha}(\mathbf{r}) + \Delta\hat{v}_x(\mathbf{r})$. Let us emphasize, however, that $\Delta\hat{v}_x(\mathbf{r})$ does not contribute to the exchange energy, omission of this term in the Kohn-Sham equation makes the local potential $v_x^{\text{AASC}\alpha}$ the approximate one. With respect to the virial relation, it follows from the definition of $v_x^{\text{AASC}\alpha}(\mathbf{r})$ given by Eq. (1) that $v_x^{\text{AASC}\alpha}(\mathbf{r})$ satisfies by construction the Levy-Perdew virial condition. Also, it is easy to show using the fact that both $E_x[\rho_\lambda] = \lambda E_x[\rho]$ and $E_{xLP}[v([\rho_\lambda]), \rho_\lambda] = \lambda E_{xLP}[v([\rho]), \rho]$ that $\alpha_x[\{\psi_i\}]$, as defined by Eq. (2), is invariant under coordinate scaling (does not depend on λ). Then using $E_x^{\text{AASC}\alpha}[\rho_\lambda] =$

$E_{xLP}[v_S([\rho_\lambda]), \rho_\lambda] + \alpha_x E_{xLP}[\tilde{v}_{\text{resp}}^0([\rho_\lambda]), \rho_\lambda]$ and the fact that $\delta E_x^{\text{AASC}\alpha}[\rho_\lambda] = \lambda \delta E_x^{\text{AASC}\alpha}[\rho]$, and following the same arguments as in Ref. [28], it can be readily shown that $v_x^{\text{AASC}\alpha}(\mathbf{r})$ also satisfies the scaling property.

In the case of the potentials introduced by Becke and Johnson [20] and Staroverov [23], it is clear that they satisfy the scaling requirement. However, the fact that these potentials do not satisfy the Levy-Perdew condition implies that the virial relation in the Born-Oppenheimer approximation [29] is not satisfied either (see Ref. [30] for details). Moreover, as a consequence of this, “there is no unique choice of functional for the evaluation of the exchange energy” for structure optimization or total energy comparison (see Ref. [31], where the Becke-Johnson potential was employed for band gap calculations in solids). Also in the case of the BJ and other model potentials discussed in [20, 23], the third requirement from [27, 28], namely, that the model potential must correspond to the functional derivative of the model functional with respect to the density is not satisfied.

We denote as in Ref. [23] by E_{conv} the total energy computed with the exact exchange expression $E_x[\{\psi_i\}]$ using the converged orbitals and by E_{vir} the corresponding one which includes the Levy-Perdew expression $E_{xLP}[v_x, \rho]$ for exchange. Since for the BJ and related potentials $E_x[\{\psi_i\}] \neq E_{xLP}[v_x, \rho]$ the total energy values E_{conv} and E_{vir} are also different. The claims that “($E_{\text{vir}} - E_{\text{conv}}$) gives an indication of how close $v_{x\sigma}$ is to the exact functional derivative” [23] or that it serves as an indication of the accuracy of the calculation itself (see Ref. [32]) do not seem to hold generally, as there are approximate KS exchange potentials (such as the AASC α one, for example), which while differing from the exact one, yield, nonetheless, $E_{\text{vir}} = E_{\text{conv}}$.

In the present article, in order to compare the results obtained using the AASC α model with those coming from the BJ and related potentials, we provide numerical values, in particular, for diatomic molecules. In order to carry out this numerical comparison, the BJ effective model potentials proposed in [20] and [23] were implemented in a fully-numerical diatomic molecule code [34] (due to its numerical instability stemming from “troublesome”, terms, a fact that was corroborated in our test calculations, the gradient-corrected model [23] was not implemented).

For completeness, we include some results obtained in the context of the GLLB model proposed in Ref. [14], the localized Hartree-Fock (LHF) model [15, 33], and the common energy denominator approximation (CEDA) [35]. We compare these results with those of the BJ and related potentials as well as with the AA-BJ ones obtained by applying the AASC α model to the BJ functional. It is shown that the AA-BJ results are only slightly improved due to this application. We also include some previous AASC α model results obtained for the PW91 and GLLB model functionals (in particular of the AA-PW91 and AA-m2 types, see Ref. [24]). These results show that all these models are closer to EXX than

the BJ or AA-BJ ones in the case of diatomic molecules.

III. RESULTS AND DISCUSSION

Table I shows the Hartree-Fock total energies and the energy differences for KS-*x-only* methods calculated when the virial relation is used (except for the “BJ(conv)” column). The energy differences of the approximate methods (eight last columns) should be compared to the exact exchange (EXX) values shown in the second column or to the KS(*x-only*) values obtained by the iterative procedure described in Ref. [36] (shown in the third column), which are very close to the EXX values.

All approximate methods shown in Table I, except for the BJ potential, are exact for the singlet state of a two-electron system (H_2 molecule). The orbital-dependent methods for the response potential term (GLLB, AA-m2, CEDA and LHF) provide very good approximations to the EXX energies, the CEDA and LHF values are only 2 mHartrees higher than the corresponding EXX energies. The AA-PW91 potential, taken here as an example of an asymptotically-adjusted potential where the response term is modeled by a conventional PW91 DFT functional was found to yield a good approximation to the EXX energy; the largest difference is 39.4 mHartrees for the F_2 molecule (as compared to the EXX difference which is 8.6 mHartrees).

The BJ differences still are significantly larger than those arising from all other approximate methods. The negative value in Table I shows that the corresponding energy is lower than the HF value, i.e. the variational principle is not satisfied. Large errors in the total energy also affect significantly the calculated atomization energies and the predicted equilibrium geometries.

The ionization potentials approximated by the highest occupied molecular orbital (HOMO) energy are presented in Table II. The situation is similar: the GLLB, AA-m2, CEDA and LHF methods provide an excellent approximation to the EXX values. The AA-PW91 values are also very close to the EXX for all molecules presented in Table except for the N_2 and FH. The BJ potential underestimates the ionization potential by an amount of ~ 30 -50%. The BJ potential is calculated without shift as suggested in [20]. By applying the shift, the HOMO energies will be equal to the corresponding HF values (but not to the OEP ones).

The asymptotically-adjusted, GLLB, CEDA and LHF exchange potentials, as well as the BJ model potential, provide an excellent approximation to the exact exchange

Kohn-Sham potential. The asymptotically-adjusted potentials based on the DFT approximation for the response term (the AA-PW91) are invariant w.r.t. unitary transformation of orbitals (as is also the BJ potential); however, the AA-m2 and GLLB ones are not. The advantages of the previously proposed AA-PW91, AA-m2 and GLLB models (and of the CEDA and LHF methods) are the following: (i) For these models $E_{\text{vir}} = E_{\text{conv}}$ (notations from [23]); these models constitute examples of situations where although $(E_{\text{vir}} - E_{\text{conv}}) = 0$, the potential is still only approximate; (ii) the energies obtained by the AA, GLLB models and by the CEDA and LHF methods satisfy the variational principle: $E^{\text{HF}} \leq E^{\text{OEP}} \leq E_{\text{vir}}^{\text{approx}}$, which is not the case for the BJ model; (iii) the virial energy for the AA and for the GLLB models is an excellent approximation to the OEP/EXX energy. This is not the case for the model potential of Refs. [20, 23], in spite of the fact that the BJ model is in excellent agreement with the OEP exchange potential; (iv) the ionization potential approximated by the HOMO energy is a property entirely defined by the effective potential. The recently proposed BJ model potential fails to adequately describe this property, in contrast with the AA-PW91, GLLB and AA-m2 models and with CEDA and LHF methods, where the agreement with the EXX values is, in most cases, excellent.

Some of the shortcomings of the model potentials from Refs. [20, 23] may be eliminated, however, by scaling the model response term by the AASC α method, as it was done in Ref. [24]. A rigorous variational justification for this type of scaling is given in Eqs. (12) through (15) of Ref. [24]. By applying this procedure to the BJ model, the new AA-BJ potential (for the spin-unpolarized case) reads

$$v_{\text{x}}^{\text{AA-BJ}} = v_{\text{S}} + \alpha_{\text{x}}[\{\psi_i\}]\sqrt{\tau[\{\psi_i\}]/\rho}, \quad (5)$$

where τ is the kinetic energy density. The self-consistent constant α_{x} is defined by

$$\alpha_{\text{x}}[\{\psi_i\}] = \frac{E_{\text{x}}[\{\psi_i\}] - E_{\text{xLP}}[v_{\text{S}}, \rho]}{E_{\text{xLP}}[\sqrt{\tau[\{\psi_i\}]/\rho}, \rho]}. \quad (6)$$

The energies for the new AA-BJ model (we emphasize that $E_{\text{vir}} = E_{\text{conv}}$ for AA-BJ) are presented in last column of Table I. The AA-BJ energies are slightly closer to the EXX values than E_{conv} values for the original BJ model (BJ(conv) column in Table I). Moreover, modified AA-BJ model eliminates the ambiguity with regard to the choice of functional for the evaluation of the exchange energy (conventional or virial). The ionization potentials presented in Table II also are slightly improved in the AA-BJ model as compared to the original BJ values.

In Table III we present some bond lengths values obtained from several different *x-only* methods. We do not include the diatomic molecule F_2 as it does not bind at the level of an *x-only* approximation. The results show that for H_2 , FH and N_2 , the AA-BJ bond lengths coincide up to three decimals with those obtained by means

TABLE I: Full-numerical Hartree-Fock (HF) total energies (in a.u.) and differences between KS-x-*only* and HF total energies (in mHartrees) calculated at the experimental geometries. ^aValues are taken from Ref. [6]. ^bFrom Ref. [24]. ^cFrom Ref. [35]. ^dFrom Ref. [33].

	HF	EXX ^a	KS(x- <i>only</i>)	AA-PW91 ^b	GLLB ^b	AA-m2 ^b	CEDA ^c	LHF ^d	BJ(vir)	BJ(conv)	AA-BJ
H ₂	-1.1336	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-80.6	0.8	0.0
FH	-100.0708	2.0	2.2	17.0	5.9	3.7			533.1	10.4	6.6
N ₂	-108.9931	5.2	5.7	30.4	11.4	8.3	7.7	7.3	239.4	9.9	9.5
CO	-112.7909	5.1	5.6	31.1	12.2	9.1	7.6	7.2	323.0	12.6	11.5
F ₂	-198.7722	8.6	9.3	39.4	16.8	13.6			1124.9	23.1	18.1

TABLE II: Ionization potential approximated by the negative of the HOMO energies (in eV). ^aFrom Ref. [5]. ^bRef. [24]. ^cRef. [6]. ^dN₂ → N₂⁺(²Σ_g). ^eN₂ → N₂⁺(²Π_u). ^fFrom Ref. [35]. ^gFrom Ref. [15].

	HF	EXX ^a	AA-PW91 ^b	GLLB ^b	AA-m2 ^b	CEDA ^f	LHF ^g	BJ	AA-BJ
H ₂	16.2	16.2	16.2	16.2	16.2	16.2	16.2	10.1	16.1
FH	17.7	17.4	13.3	16.5	18.2			9.4	11.0
N ₂ ^d	17.3	17.2 ^c	12.7	15.5	17.0	17.1		9.9	10.4
N ₂ ^e	16.7	18.1 ^c	13.9	16.2	18.0	18.5		10.7	11.2
CO	15.1	14.1	11.1	13.7	15.0	15.0	15.0	8.4	9.0
F ₂	18.2	14.5	13.4	15.9	18.7			9.3	11.1

of the exact Kohn-Sham x-*only* method. For the case of CO, there is a difference of 0.002 angstroms between the AA-BJ and the KS(x-*only*) result. The BJ(vir) geometries differ from the KS(x-*only*) results for all four diatomics presented in Table. The BJ(conv) bond lengths coincides with the exact KS(x-*only*) results for the case of N₂, and differ for other molecules.

IV. CONCLUSIONS

All potentials discussed here have the same structure: they comprise a Slater potential plus a modeled response term. As a result, the computational cost for all models is approximately the same, except that for the AA-PW91, GLLB, AA-m2, CEDA, LHF cases, where an additional

exact-exchange energy term has to be calculated. The same term, however, must also be calculated for the BJ model potential when the total energy is obtained not by means of the virial relation, (where it is denoted as E_{vir} in Ref. [23]), but through the exact exchange term (in which case, it is denoted as E_{conv}). The AASCα method is a simple procedure which permits to transform the BJ model potential into a new AA-BJ potential which satisfies the Levy-Perdew virial relation without increasing the computational cost (in fact, this procedure may be applied to model potentials of any structure without reducing computational efficiency). However, the calculated AA-BJ values show only a slight improvement on the BJ ones, except for the bond lengths, which are in excellent agreement with the KS x-only results.

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TABLE III: Bond lengths (in angstroms) obtained from different *x-only* methods.

	HF	KS(<i>x-only</i>)	BJ(vir)	BJ(conv)	AA-BJ
H ₂	0.734	0.734	–	0.732	0.734
FH	0.897	0.896	0.860	0.895	0.896
N ₂	1.065	1.065	1.066	1.065	1.065
CO	1.102	1.101	1.086	1.099	1.099

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